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Multiple Eluent and pH Effects on Ion Chromatography of Phosphate and Arsenate

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Abstract

The ion-exchange separation theory of Mayer and Tompkins is extended to the case of multiple eluent ions. The selectivity coefficients for carbonate and hydroxide, each relative to bicarbonate, were estimated from retention data for bromide and sulfate. These results were used to interpret the chromatographic retention data for phosphate and arsenate as a function of pH in carbonate-bicarbonate eluents. Despite large relative errors in the empirical constants, the qualitative behavior of the polybasic anions was accounted for by the predominant effect of the triply charged ions on the retention time, even at low relative concentrations.

Analytical applications of ion-exchange chromatography have increased markedly (*1, 2*) since the development of practical conductimetric detection through the application of a suppressor column to reduce the contribution from the eluent (*3*). In this system a preferred eluent for the determination of anions is a mixture of sodium carbonate–sodium bicarbonate (*2*). Varying proportions of these components have been recommended for special applications, e.g., the determination of arsenate (*4*), and other mixed eluents have been proposed for the determinations of the anions of weak acids by ion chromatography (*5*). A quantitative description of the role of individual eluting anions in such mixtures, therefore, is of some interest in determining the optimum proportions for particular analytical problems.

In their original paper on ion chromatography, Small et al. (*3*) noted that the relative elution time of phosphate differed in various eluents and ascribed the effect qualitatively to the relative proportions of protolytic species of phosphate at the respective hydrogen ion concentrations (pHs). Previously,

Beukenkamp et al. (*6*) had studied the ion-exchange chromatography of phosphate and polyphosphates and developed equations for the effect of pH on the elution times of tri- and tetraprotic acids with a single effective eluent ion.

This paper presents an elementary treatment of multiple ionic eluents and mutual effects of pH and varying proportions of carbonate and bicarbonate on the elution of phosphate and arsenate. Preliminary data on the latter analytes were interpreted on the basis that carbonate was the sole effective eluent (*7*).

The theoretical treatment is derived from the following four premises.

1. Basic elution (*8*) is expressed by

$$U^* = D_A \tag{1}$$

where U^* is the reduced elution volume, i.e., the volume of eluent needed to move analyte from the entrance of the separator column to maximum concentration at the detector, exclusive of eluent initially in the system in nonseparative segments and in the voids of the separator, divided by the bulk bed volume of the exchange resin. D_A is the volumetric distribution coefficient of the analyte, i.e., the equilibrium ratio of adsorbed equivalents per cubic meter of exchange resin divided by equivalents per cubic meter in the solution phase. Equation (1) was derived by Mayer and Tompkins (*8*) for the case of an infinite number discrete separator stages (plates) but has been accepted as a reasonable approximation to actual continuous exchange conditions (*9, 10*).

2. Stoichiometric exchange occurs between ionic species of different formal charge. This premise is a consequence of electroneutrality.

3. The exchange capacity of the separator column is saturated by the eluent ions. Although the concentration of analyte ions in the developing front may be the same order as that of the eluent species, the analyte is neglected in the overall stoichiometry of the column.

$$Q = \Sigma_i \, i[E_i] \tag{2}$$

where Q is the total exchange capacity (g-equiv./m^3 of bed volume) and $[E_i]$ is the concentration of the ith *eluent* species on the resin, having charge i, in the same units as Q.

4. For every pair of ionic species in the system, there is a constant selectivity coefficient corresponding to the concentration equilibrium for the exchange reaction

$$A_i^j + (i/j)Rj \cdot B^j \rightleftharpoons R_i \cdot A^i + (i/j)B^j \tag{3}$$

where R represents the exchange resin functional group.

$$k_{AB} = \frac{[A_i]}{A_i} \left(\frac{B_j}{[B_j]} \right)^{(i/j)} \tag{4}$$

where brackets, as in Eq. (2), represent the concentration of resin-bound species and unbracketed letters represent the corresponding solution-phase concentrations. k_{AB} will be used conventionally for the selectivity coefficient of analyte A with respect to eluent B. To emphasize that Eq. (2) is restricted to eluents, the symbol x_{ij} will be used for the selectivity coefficient for eluent species i and j. To limit the number of sub- and superscripts, lower-case subscripts will be used to identify a species and also as a summation index, whereas lower-case superscripts will represent the formal charge and will be used as exponents.

$$x_{ij} = \frac{[E_i]}{E_i} \left(\frac{E_j}{[E_j]} \right)^{(i/j)} \tag{5}$$

For n total ionic species, the $n - 1$ relations of Eq. (4) and Eq. (2) permit solution of Eq. (1) in terms of solution concentrations. If ionic charges no greater than 2 are involved, the equations of highest degree are quadratic and explicit solutions are readily obtained. For example, consider a bivalent analyte ion A_2 and three eluent ions E_1, E_2, and E_3, where E_1 and E_3 are univalent and E_2 is bivalent.

From Eq. (2),

$$Q = [E_1] + 2[E_2] + [E_3] \tag{6}$$

The concentrations of $[E_2]$ and $[E_3]$ on the resin phase are expressed in terms of $[E_1]$ through the corresponding selectivity coefficients (Eq. 5):

$$[E_2] = E_2 x_{21} [E_1]^2 / E_1^2 \tag{7}$$

$$[E_3] = E_3 X_{31} [E_1] / E_1 \tag{8}$$

The quadratic equation obtained by substituting Eqs. (7) and (8) in (6) has the solution

$$[E_1] = (b/2a)[(1 + m)^{1/2} - 1] \tag{9}$$

where

$$a = 2x_{21} E_2 / E_1^2 \tag{10}$$

$$b = (E_1 + x_{31} E_3)/E_1 \tag{11}$$

$$m = 8x_{21} Q E_2 / (E_1 + x_{31} E_3)^2 \tag{12}$$

From Eq. (1),

$$U_2^* = D_A = k_{21}[E_1]^2/E_1^2 \tag{13}$$

substituting the equivalent expression for the analyte distribution coefficient,

$$D_i = k_{ij}D_j^{(i/j)} \tag{14}$$

Substitution of Eq. (9) for $[E_1]$ yields

$$U_2^* = \frac{k_{21}}{x_{21}^2} \quad \frac{(E_1 + x_{31}E_3)^2}{8E_2^2}[1 + (m/2) - (1 + m)^{1/2}] \tag{15}$$

Similarly, for a univalent analyte,

$$U_1^* = \frac{k_{11}}{x_{21}} \quad \frac{(E_1 + x_{31}E_3)}{4E_2}[(1 + m)^{1/2} - 1] \tag{16}$$

For easier application, Eqs. (15) and (16) can be put into linearized form:

$$U_2^*E_2 = \frac{k_{21}Q}{2x_{21}} + \frac{k_{21}^{1/2}}{2x_{21}}(U_2^{*1/2}E_1) + \frac{k_{21}^{1/2}x_{31}}{2x_{21}}(U^*{}_2{}^{1/2}E_3) \tag{17}$$

and

$$(U_1^*)^2E_2 = \frac{k_{11}^2Q}{2x_{21}} - \frac{k_{11}}{2x_{21}}(U_1^*E_1) - \frac{k_{11}x_{31}}{2x_{21}}(U_1^*E_3) \tag{18}$$

respectively.

The extension of the above equations for multiple eluent ions to an analyte that undergoes protolysis is straightforward and follows the treatment of Beukenkamp et al. (*6*). If the protolytic reactions occur at least as fast as the ion-exchange reactions, the analyte must elute as a single component because the protolytic species are in a constant proportion determined by the pH of the eluent. Equation (1) becomes

$$U^* = \Sigma_i[A_i]/\Sigma_i A_i \tag{19}$$

The concentration of any of the analyte species can be expressed in terms of any other through the protolytic constants

$$A_1^{-i} = K_i A_i^{-(i-1)}/H^+ = H^+ A_i^{-(i+1)}/K_{i+1}, \text{ etc.} \tag{20}$$

and

$$\Sigma_i A_i = A_k/f_k \tag{21}$$

where, for a triprotic acid,

$$f_0 = H^3/(H^3 + H^2K_1 + HK_1K_2 + K_1K_2K_3)$$
$$f_1 = H^2K_1/(H^3 + H^2K_1 + HK_1K_2 + K_1K_2K_3) \quad (22)$$
$$f_2 = HK_1K_2/(H^3 + H^2K_1 + HK_1K_2 + K_1K_2K_3)$$

etc.

From Eq. (14),

$$[A_i] = A_i k_{ij} D_j^{(i/j)} \quad (23)$$

Hence,

$$U^* = \Sigma_i A_i k_{ij} D_j^{(i/j)} / \Sigma_i A_i \quad (24)$$

For each term in the numerator there is a corresponding representation of $\Sigma_i A_i$ in the denominator in terms of A_i, hence

$$U^* = \Sigma_i k_{ij} f_i D_j^{(i/j)}$$

Note that D_j is the distribution coefficient for one eluent species, j. It is immaterial which is selected provided k_{ij} is determined relative to the same eluent species.

This result is equivalent to Eqs. (19) and (20) of Ref. *6* for a single eluent. The distribution coefficients for each eluent ion must be evaluated independently with single analyte species. Then the selectivity coefficients for the protolytic species can be evaluated from a linear regression of retention volume at various pHs (which determine the f_i's explicitly).

EXPERIMENTAL

A Dionex Model 10 Ion Chromatograph was used in conjuction with a 150×3 mm precolumn (part no. 30232) and a 500×3 mm Anion Separator (part no. 30170). The flow rate was set at 30% of pump capacity and was measured as 2.51 mL/min. The bed volume was calculated as 4.594×10^{-6} m^3 for a length of 650 mm. The void volume of the separator was taken to be 38% of the bed volume (*9*). The liquid volume in the remainder of the system was determined by bypassing and pre- and separator columns with 0.5-mm i.d. Teflon tubing. The total exchange capacity of the column was estimated by equilibrating the separator columns with 0.01 *M* NaOH, washing with deionized water until the eluent reached pH < 7, and passing exactly 25 mL of standardized 0.01 *M* HCl through the columns. The eluent plus deionized water needed to rinse to pH > 5 was collected and

titrated. The loss in acid titer was accounted for as exchange of Cl^- for OH^- on the resin, leading to an exchange capacity of 43 g-equiv./m^3. This may be compared to the manufacturer's estimate of 0.03 meg/g dry weight. Elution times were determined from the chart record obtained with a Hewlett-Packard 7101B Strip Chart Recorder operating at 0.5 to 2 in./min.

Analyte injections used the original 0.1 mL injection loop and concentrations of 100 ppm of the anion. Three different series of eluents, used over a period of 8 months, consisted of varying proportions of carbonate, bicarbonate, and pH. The pH of each was measured with a Leeds & Northrup Model 7421 pH Meter and Fisher 13-639-92 combination glass electrode calibrated at pH 6.86 and 9.18 with Beckman buffers. The total alkalinity of each eluent was determined by titration to pH 4.5 with HCl by standard procedures (*11*). The actual concentration of each eluent anion was calculated from the relations:

$$t = \text{total alkalinity by titration}$$
$$h = OH^- = 10^{(pH - 11.0)}$$

TABLE 1

Experimental Data. Eluents and Reduced Retention Volumes

		Alkalinity t	HCO_3^- E_1	CO_3^{2-} E_2	OH^- E_3	U^*			
No.	pH	(units, g-equiv./m^3)				Br	SO_4	PO_4	AsO_4
1-1	8.7	19.9	19.02	0.42	0.01	3.01	8.64	3.45	3.89
1-2	9.0	10.2	9.36	0.44	0.01	4.16	15.09	5.36	6.34
1-3	10.0	15.7	7.69	3.94	0.11	2.23	2.90	1.29	1.56
1-4	10.0	10.4	5.30	2.48	0.10	2.74	4.27	1.59	2.47
1-5	11.0	11.3	1.00	4.66	1.00	2.30	3.07	2.25	5.14
1-6	11.1	7.4	0.50	2.83	1.20	2.93	5.03	4.49	10.82
1-7	9.9	2.8	1.62	0.57	0.08	4.92	16.40	7.00	13.78
1-8	10.2	4.6	1.75	1.36	0.17	3.61	8.53	4.05	8.09
2-1	8.9	10.3	9.54	0.37	0.01	4.54	13.88	4.76	8.64
2-2	10.0	5.6	2.83	1.35	0.10	4.87	10.88	4.43	8.20
2-3	10.9	5.3	0.58	1.98	0.72	4.21	12.36	10.50	31.94
2-4	9.3	2.8	2.35	0.24	0.02	6.56	—	10.00	—
2-5	11.9	25.1	0.21	8.30	8.32	3.39	3.61	7.88	13.83
2-6	11.0	9.0	0.72	3.59	1.07	3.50	5.80	8.45	19.46
3-1	11.2	8.2	0.40	3.10	1.64	3.83	8.26	17.16	
3-2	9.9	11.5	6.32	2.55	0.09	1.54	2.58	4.27	
3-3	9.6	5.8	4.35	0.73	0.04	3.83	9.40	3.39	
3-4	9.6	2.8	2.00	0.39	0.04	5.47	20.88	8.42	
3-5	9.7	13.5	8.91	2.29	0.06	2.52	4.10	1.32	
3-6	9.4	11.2	9.17	1.00	0.02	3.23	7.66	2.41	

$$c/b = 10^{(\mathrm{pH} - 10.33)}$$
$$b = \mathrm{HCO_3^-} = (t - h)/[1 + 2(c/b)]$$
$$c = \mathrm{CO_3^{2-}} = b(c/b)$$

all units g-equiv./m^3.

The compositions of the eluents and the reduced elution volumes for bromide, sulfate, phosphate, and arsenate analytes are summarized in Table 1.

RESULTS AND DISCUSSION

The intereluent selectivity coefficients, x_{21} and x_{31}, express the resin selectivity for carbonate and hydroxide, respectively, each relative to bicarbonate. These coefficients were determined from the elution data for the simple analyte anions, bromide and sulfate, by a least-squares multivariate fit to the linearized Eqs. (18) and (17), respectively, using an ortho-normal algorithm. The fitted constants and their standard deviations are shown in Table 2. The derived parameters were calculated from these coefficients and the corresponding standard deviations were estimated by error-propagation formulas (*12*). Because a linearized equation does not necessarily provide the best fit of independent parameters, the nonlinear eqs. (15) and (16) were also fitted to the data by the simplex search algorithm (*13*), minimizing the sum of squares of differences between calculated and measured U^*. The independent variables were k_{11}/x_{21}, x_{21}, and x_{31} in Eq. (16) and k_{21}/x_{21}^2, x_{21}, and x_{31} in Eq. (15). The simplex was started from at least two different positions to avoid false minima. Because the first two variables appeared

TABLE 2

Ion-Exchange Parameters and Their Standard Deviations

Analyte	n	X_{21}	X_{31}	k_{11}	k_{21}	k_{31}	s_U[c]
Br	20	2.3 ± 1.9	-8.4 ± 3.7	1.5 ± 0.7			7.2
Br[a]	19	1.2 ± 0.8	(0)[b]	1.2 ± 0.5			9.8
Br[d]	19	1.8	−0.03	1.3			0.9
SO_4	19	3.4 ± 3.1	-5.9 ± 3.0	2.3 ± 1.9			3.7
SO_4[a]	18	2.2 ± 1.8	(0)[b]		1.6 ± 1.2		4.8
SO_4[d]	19	4.1	0.4		2.2		2.9
PO_4	20	(1.7)	(0)[b]	59 ± 28	0.12 ± 0.07	22 ± 3	2.3
AsO_4	13	(1.7)	(0)[b]	180 ± 120	-0.03 ± 0.31	9.0 ± 1.4	4.9

[a]Omitted Eluent 2-5; apparent outlier.
[b]Values in parentheses were arbitrarily fixed.
[c]Standard deviation of fit of reduced retention time.
[d]Simplex iterative fit to nonlinear Eqs. (15) and (16).

highly correlated, minima lay in narrow troughs and final covergence was slow. The resulting values lay within the error limits found for the linearized solutions and could not be said to be more accurate, except for x_{31}. The linear equations indicated apparently significant negative values for x_{31}. This result, which has no physical meaning, apparently was an artifact of the linearization because the simplex solutions of the nonlinear equations gave small positive or essentially zero values.

For analysis of the phosphate and arsenate data, x_{31} was arbitrarily set at zero, representing completely negligible eluent power for hydroxide. The corresponding value for x_{12} was chosen at 1.7. The linear Eq. (25) was fitted to the reduced retention times for phosphate and arsenate, using protolysis constants from Baes and Mesmer (*14*). The reference eluent species, j, was bicarbonate and values of D_1 were calculated from the ratio of $[E_1]$ (Eq. 9) to E_1 (experimental). The results are shown in Table 2.

The statistical approach used here and the relatively narrow range of eluent conditions accessible to measurement without stripping the suppressor column lead to rather imprecise estimates of the exchange parameters. In particular, k_{21} could not be estimated for arsenate. With the pH range of the experiments, the bivalent anions of both phosphate and arsenate were the overwhelmingly predominant species. Nevertheless, the relative magnitudes of the derived selectivity coefficients are consistent. The relatively poor precision of the derived selectivity constants undoubtedly can be attributed largely to the use of concentration equilibrium constants for exchange. Inczedy (*15*) and Salmon (*16*) have shown that activity coefficient effects are especially significant for anions of different charges.

It should be noted that the relative reduced retention volumes of the simple analytes, bromide and sulfate, vary markedly with eluent composition. At the highest alkalinity (Eluent 2-5, Table 1) they are nearly equal, whereas at the lowest alkalinities (Eluent 1-7 and 3-4) the retention volume of sulfate is nearly 4 times that of bromide. Similarly, Jenke (*17*) has reported that the order of elution of nitrate and sulfate can be reversed by varying the proportions of carbonate/bicarbonate in the eluent. This striking effect is not a consequence of varying pH but of different proportions of uni- and bivalent ions on the elution of analyte ions of different charge type.

Rounded values of the experimental selectivity coefficients for phosphate and arsenate were used to calculate expected retention times for a range of total alkalinity and pH of carbonate buffers. These results are plotted in Fig. 1 and 2. Retention times were calculated for the flow and separator column conditions of these experiments. The figures show the expected qualitative properties. At low pH, retention times are long because of the high

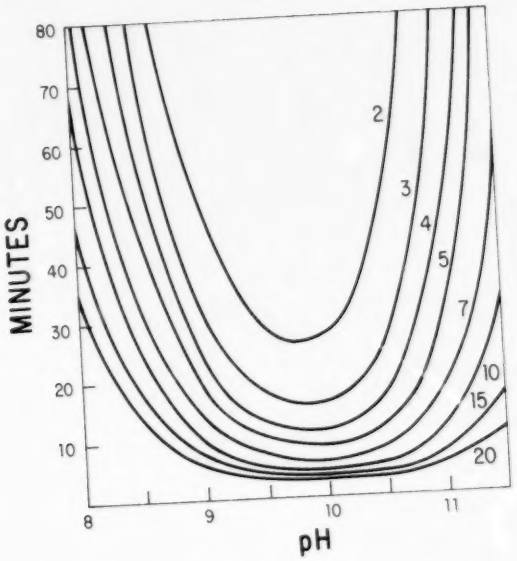

FIG. 1. Calculated retention times of phosphate as a function of pH at constant total alkalinity of carbonate-bicarbonate eluents. Numbers on curves indicate total alkalinity in units of mg $CaCO_3$/L.

proportion of bicarbonate in the eluent, whereas at high pH the higher proportions of triply-charged analyte ions increases the retention time. At all pHs, increasing the total alkalinity of the eluent reduces retention time. The arsenate data are shifted to slightly lower pH than the corresponding times for phosphate and show a greater dependence on total alkalinity. Expected retention times for the experimental eluents were read from the figures and compared to the observed values to give standard deviations of 4.6 min for phosphate and 9.1 min for arsenate. These error estimates are somewhat larger than the statistical values from the least-squares fit (Table 2) through the inclusion of the error of reading the figures as well as that due to rounding off the constants.

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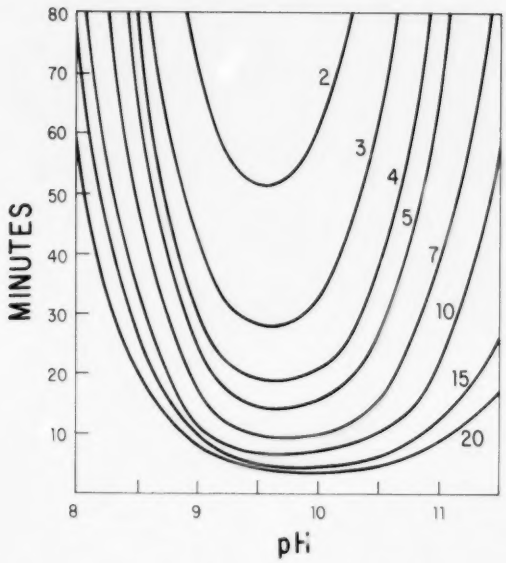

FIG. 2. Calculated retention times of arsenate as a function of pH at constant total alkalinity of carbonate-bicarbonate eluents. Numbers on the curves indicate total alkalinity in units of mg $CaCO_3$/L.

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